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The Inventor of this invention in the sense of being the deviser thereof within the meaning of Section 16 of the Patents Act 1949, is:—WULF VON BONIN, of 9 Goethestrasse, Leverkusen, Germany, of German nationality.

COMPLETE SPECIFICATION

Water-in-Oil Emulsions

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate, organised under the laws of Germany of Leverkusen, German, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of water-in-oil emulsions the oil phases of which may contain polyesters and/or polymerisable monomers and/or inert organic solvents, in which special emulsifying agents soluble in the oil phase are used for the preparation of these reverse emulsions.

The possibility of incorporating water in solutions of unsaturated polyesters in solvents not miscible with water to form reverse emulsions has already been disclosed in German Auslegeschrift 1,150,524. This process works without the use of emulsifying agents soluble in the oil phase. However, it has been found that without the use of such auxiliary agents, it is only possible to produce water in oil emulsions of relatively low water contents of about 50 to 200% calculated on the oil phase of the reverse emulsion.

It has further been proposed to employ graft polymers of vinyl esters, aromatic vinyl compounds or acrylates or methacrylates on polyalkylene oxides as emulsifying agents for the preparation of water in oil emulsions of polyesters or solutions of polyesters in solvents that are not miscible with water. Even if these graft polymers are effective water in oil emulsifiers, they generally have the property of not dissolving in polyesters, especially if the poly-

esters are unsaturated. They can therefore only be employed in relatively dilute solutions of these polyesters in a solvent for the polymer.

It has been found that for the preparation of water-in-oil emulsions the oil phases of which may contain saturated and/or olefinically unsaturated organic polyesters and/or polymerisable monomers containing at least one terminal $\text{CH}_2=\text{C}<$ group and a liquid inert organic solvent, it is especially advantageous to use as emulsifying agent, derivatives of polyesters of polyhydric, especially dihydric, alcohols and polybasic, especially dibasic, carboxylic acids, which derivatives contain polyalkylene oxide radicals linked through their terminal hydroxyl and/or carboxyl groups.

The present invention thus provides a water-in-oil emulsion having water finely dispersed within a liquid organic phase, said organic phase comprising in a quantity of 1 to 100% by weight of water insoluble or sparingly soluble emulsifying agent which is a reaction product which has a molecular weight of 1,000 to 20,000 of a polyester which has a molecular weight of 500 to 10,000 of an organic compound containing at least two hydroxyl groups and an organic carboxylic acid containing at least two carboxyl groups, said polyester having at least one terminal carboxyl group and/or at least one terminal hydroxyl group, and a water-soluble polyalkylene oxide which has a molecular weight between 400 and 10,000.

The said polyester derivatives are derived from polyesters of molecular weight 500 to 10,000, preferably 1000 to 5500, and the water-soluble polyalkylene oxides have a mole-

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cular weight of 400 to 10,000, preferably 1000 to 4000.

The said polyester derivatives, which are used as emulsifying agent have a molecular weight between 1,000 and 20,000, are insoluble or sparingly soluble in water. By the term "sparingly soluble or insoluble" we mean substances which are soluble in water at 25° C. up to an amount of 10 grams per 100 grams of water.

In particular it is preferred that the water insoluble emulsifying agent be a water insoluble derivative of a water insoluble polyester of a dihydric alcohol and a dibasic carboxylic acid, said polyester having molecular weight of 500 to 10,000 and having at least one terminal carboxyl and/or at least one hydroxyl group, the hydrogen atom of said terminal groups being replaced by a radical which is obtained by removal of a hydroxyl group from the molecule of a water soluble polyethylene oxide having a molecular weight between 400 and 10,000 and the molecular weight of said emulsifying agent being from 1,000 to 20,000.

The polyalkylene oxide radicals are linked to a hydroxyl and/or carboxyl groups of the polyesters either directly but preferably indirectly through polyfunctional connecting members.

According to a further embodiment of the invention, there is provided a water-in-oil emulsion having water finely dispersed within a liquid organic phase said liquid organic phase comprising 1) a liquid organic polyester devoid of aliphatic unsaturation, a liquid olefinically unsaturated organic polyester, a liquid olefinically unsaturated organic monomer containing at least one terminal $\text{CH}_2=\text{CH}<$ group, a liquid organic solvent devoid of aliphatic unsaturation, a liquid solution of a polyester in said liquid olefinically unsaturated monomer, or a liquid solution of a polyester in said liquid organic solvent devoid of aliphatic unsaturation, said phase (1) being devoid of emulsifying properties and 2) an emulsifying agent as defined in any of claims 3 to 5 which emulsifying agent is dissolved in said organic phase.

Suitable polymerisable monomers containing at least one terminal $\text{CH}_2=\text{C}<$ group, include more especially monovinyl aromatic compounds such as styrene or its derivatives and substituted products such as styrenes alkylated in the nucleus or in the side chain and halogenation products thereof, as well as aliphatic vinyl compounds, for example vinyl esters such as vinyl acetate, propionate and butyrate; esters of acrylic and/or methacrylic acids such as methyl acrylate, methyl methacrylate, ethyl methacrylate and cyclohexyl methacrylate as well as vinyl halides such as vinyl chloride or vinylidene chloride, and monoolefines and/or polyolefines, in particular aliphatically conjugated diolefines, such as isoprene, 2,3-dimethyl butadiene, chloroprene as well as

acrylonitrile and mixtures thereof are also suitable.

The term "inert solvents" as used herein is meant to relate to those organic solvents, which show no reaction under normal conditions with polyesters, polymerisable monomers, compounds with methylol groups, isocyanates, compounds with epoxy groups and which do not interfere with the course of the polymerisation. Suitable inert solvents are for example liquid esters of aliphatic carboxylic acids having 1-6 carbon atoms with monohydric alcohols having 1-6 carbon atoms, aromatic hydrocarbons such as benzene, toluene and xylene, aliphatic ethers such as glycol dimethyl ether, glycol monomethyl ether acetate and halogenated aliphatic hydrocarbons such as chloroform, carbon tetrachloride and per- and trichloroethylene.

The said polyesters are obtainable in known manner by polycondensation of di- or polybasic carboxylic acids and compounds having two or more hydroxyl groups. Examples of suitable di- or polybasic carboxylic acids are especially aromatic, cycloaliphatic, saturated and unsaturated aliphatic carboxylic acids such as phthalic acids, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acids, succinic acid, glutaric acid, adipic acid and homologues, maleic acid, fumaric acid and HET acid (Hexachloro-endomethylene-tetrahydrophthalic acid). As compounds having at least two hydroxyl groups it is preferred to use dihydric aliphatic, cycloaliphatic or araliphatic alcohols such as mono-, di- or triethylene glycol or 1,2- and/or 1,3-propylene glycol, 1,3- and/or 1,4-butanediol, 1,6-hexanediol, 1,4-butanediol, 1,4-butanediol, cyclohexanediols, bis-hydroxyethyl-ester of terephthalic acid and partially etherified or esterified polyhydric alcohols such as monoallylglyceric ether, monoallylether or trimethylolpropane and monoesters of glycerol with fatty acids containing 8 to 20 carbon atoms (for example ricinoleic acid, linolenic acid, linoleic acid, stearic acid and oleic acid). It is also possible to employ as diol components phenols such as hydroquinone resorcinol or 4,4'-dihydroxydiphenylmethane 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenylsulphone and dihydroxyethyl derivatives of these compounds.

The polyesters used as starting components for the preparation of the emulsifying agents should be insoluble in water, have no significant surface active properties and be soluble in monomeric liquid vinyl compounds, especially styrene. The last-mentioned property is important especially if unsaturated polyesters together with monomeric vinyl compounds, which are subsequently to be polymerised together, are employed in the oil phase of the reverse emulsions.

The polyalkylene oxides employed for the preparation of the compounds which have an emulsifying effect to form a water-in-oil emul-

sion should have molecular weights of 400 to 10,000, preferably 1000 to 4000, and be soluble in water. Polyethylene oxides, which may if desired be partially further reacted, e.g. etherified or esterified polyethylene oxides, are therefore preferably employed, provided their polyalkylene oxide chain has the required molecular weight and the products are water-soluble. However, polyalkylene oxide copolymers are also suitable provided they meet the above-mentioned conditions, e.g. propylene oxide-ethylene oxide copolymers having a propylene oxide content below 50 mols. per cent.

The direct introduction of the polyalkylene oxide radicals into the polyester can be carried out in known manner by addition of one or more alkylene oxides to the OH or COOH groups of the polyester by acid or preferably basic catalysis. To effect this, the polyesters are reacted, for example in the presence of pyridine, or as an alkali metal salt or alcoholate with the alkylene oxides, if desired under pressure.

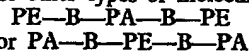
It is preferred, however, to link the polyalkylene oxide radical to the polyester molecule through a connecting member which is at least bifunctional. The connecting member should be of such a structure that it can react both with the end groups of the polyester and with the end groups of the polyalkylene oxide. Compounds which are suitable for use as such connecting members which are at least bifunctional are compounds which contain several methylol groups, methylol groups etherified with lower alcohols, isocyanate groups or epoxy groups.

Suitable compounds having several methylol or etherified methylol groups are phenol formaldehyde condensation products having at least 2 methylol groups in soluble in organic solvents, or products of etherification of these condensation products, with methyl-, ethyl-, propyl- and butyl alcohol, and aminoplasts having at least 2 methylol groups soluble in organic solvents, e.g. formaldehyde condensation products of urea, thiourea, ethylene- or propylene urea and of aminotriazines such as melamine and of guanidine and their ethers with alcohols such as methyl-, ethyl-, propyl- and butyl alcohol.

Especially suitable compounds having several isocyanate groups are aliphatic, aromatic or araliphatic diisocyanates such as hexamethylene diisocyanate, 2,4- and 2,6-toluylene diisocyanate and mixtures thereof, naphthalene-1,5-diisocyanate, 4,4'-diphenylmethane diisocyanate and triphenylmethane-4,4',4''-triisocyanate. As examples of suitable compounds having several epoxy groups may be mentioned the glycidic ethers, especially diglycidic ethers of aliphatic or cycloaliphatic polyhydric alcohols such as diglycidic ether of ethylene glycol and 1,4-butylene glycol, the triglycidic ethers of glycerine and trimethylol propane, but in particular those of polyhydric

phenols such as 4,4'-dihydroxy-diphenyldimethylmethane, 4,4'-dihydroxy-diphenyl sulphone, hydroquinone and resorcinol.

The preparation of the emulsifiers employed according to the invention may be carried out by mixing the above mentioned components, if desired in the presence of a solvent inert to isocyanates, epoxides or methylol compounds, at room temperature and then reacting them with each other at 30 to 130° C., a homogeneous product being formed. Suitable inert solvents are esters of aliphatic carboxylic acids with monohydric alcohols such as ethyl acetate, aromatic hydrocarbons such as benzene, aliphatic ethers such as glycol dimethyl ether, halogenated aliphatic hydrocarbons such as chloroform. The reaction should generally be carried out in such a manner that there is no appreciable rise in viscosity of the reaction mixture during the reaction, i.e. there should on the whole be no polyaddition or polycondensation during the reaction but ideally the molecules of the reactants should only react singly with each other. Reaction products should thus preferably have the following structure: Polyester molecule (PE)-connecting member (B)-polyalkylene oxide molecule (PA). However, when the three components are reacted together it is impossible to prevent the formation of other types of molecules such as



or PE-B-PE-B-PA. To keep the molecular weights of the resulting reaction products as low as possible, it has been found advantageous to employ the polyester components in molar excess over the two other components. The above-mentioned components are preferably employed in the following proportions: 2-11 mols. of polyester, 1 mol. of polyalkylene oxide, 0.5 to 2.5 mols. of the compounds having several isocyanate, epoxy or methylol groups. Although products having an inverse emulsifying effect are also obtained if proportions other than those mentioned are employed, this emulsifying effect will then usually only be manifested to a small extent or the products will be highly viscous to solid and in part will be only sparingly soluble substances and difficult to handle.

To prepare the water in oil emulsions with the aid of the emulsifying agents employed according to the process, these emulsifying agents are dissolved in quantities of 1 to 100% by weight in the oil phase which is to be emulsified; thus in the extreme case, the emulsifying agent itself functions as oil phase.

Normally, however, the oil phase consists of a polyester of any molecular weight, which is liquid at room temperature, or of solutions of polyester in inert solvents that are sparingly soluble or insoluble in water or of mixtures of polyesters and polymerisable monomers containing at least one terminal $\text{CH}_2=\text{C}<$ groups, or of polyesters, said polymerisable

monomers and solvents, or of solvents. Preferably, the oil phase consists of a saturated or unsaturated organic polyester and polymerisable monomers such as styrene, methylmethacrylate.

The polyesters contained in the oil phase have to meet the same requirements as the polyesters which serve as starting materials for the preparation of the emulsifying agents.

- 10 The above remarks also apply to their possible composition. There are in principle no limitations on the polyester content of the oil phase and it may vary between 0 and 100% minus the emulsifying agent although it is to be regarded as an advantage of the process of the invention that the polyester content of the oil phase may be above 30% without any incompatibility with the emulsifying agent being observed. If the oil phase is to be subjected to a radical polymerisation and accordingly contains compounds capable of radical polymerisation, polymerisation activators may be added to it. These activators may be the usual peroxidic, nitrogen-containing or metal compounds. They have been fully described in U.K. Patent Specifications Nos. 928,621 and 962,699.

- 30 To prepare the water in oil emulsion, the aqueous phase is stirred into the oil phase which contains the emulsifying agent according to the invention. To obtain a water in oil emulsion, the aqueous phase has to be introduced carefully, if possible portionwise, because it has been found that in the case of more highly viscous oil phases, mechanical difficulties are encountered in incorporating the aqueous phase owing to the fact that with increasing viscosity of the water in oil emulsion, the aqueous phase is taken up more and more slowly. A too great excess of aqueous phase which is not yet emulsified into the system may increase the shearing forces within the stirred mass to such an extent that separation of the system to be emulsified into the aqueous phase and the phase of reverse emulsion having a lower water content takes place, which is not desirable. The aqueous phase may

consist of pure water or aqueous solutions or suspensions. It may contain up to 60% by weight of organic water-soluble compounds such as methanol, ethylene glycol, glycerol, triethanolamine or salts such as sodium acetate, CaCl_2 , ammonium borate, sodium silicate, lead acetate or potassium persulphate or ammonium persulphate; large additions of phosphoric acid or silicic acid may also be contained in the aqueous phase. The said additions to the aqueous phase will naturally as a rule be employed in small quantities, for example if they are polymerisation activators. Moreover, the extent to which the additions to the aqueous phase influence the stability of the water in oil emulsions differs for different oil phases so that in any particular case it is necessary to determine which additives and which quantities of these additives will not prevent the formation of a water in oil emulsion.

The water in oil emulsions may contain 10 to 1500, preferably 50 to 500 volumes per cent of aqueous phase (based on the oil phase). The additional incorporation of solids is also possible, especially in the case of polymerisable emulsions before the polymerisation process. Particularly suitable solid materials are fibres or fabrics of an inorganic or organic nature.

Special effects can be achieved by the addition of soluble or pigment dyestuffs to the aqueous or oil phase of the water in oil emulsions.

The water in oil emulsions can be employed as lubricants, as hydraulic liquids or, if they contain compounds capable of radical polymerisation, for the production of polymers from the water in oil emulsions.

The following Tables firstly give details of the different properties of various polyesters which may be used in the process of the invention and secondly present Examples 1—14 in tabular form illustrating the preparation of the emulsifying agents and Examples 15 to 32 in tabular form illustrating the invention. Examples 33—42 further illustrate the invention.

The following polyesters are used to illustrate the different properties of the different types of polyesters which can be used as starting materials for the preparation of the emulsifying agents in the examples given:

Polyester	Molecular weight	% OH	% COOH	Composition in mol %
A	2000	1.7	<0.2	~49.5 adipic acid ~50.5 diethylene glycol
B	1000	3.3	<0.4	~49 adipic acid ~51 diethylene glycol
C	2200	<0.2	4.1	Polyester A, end groups reacted with maleic acid anhydride
D	2100	~1.5	~2	Polyester A, half the end groups reacted with maleic acid anhydride
E	5000	~0.3	~0.9	50 adipic acid, 35 propylene glycol, 15 butanediol
F	4000	0.9	<0.3	24 adipic acid, 25 maleic acid, 25 1,4-butanediol, 26 glycol monoricinoleate
G	5000	~0.5	~0.7	25 terephthalic acid, 25 adipic acid, 25 hexanediol, 25 1:2-propylene glycol
H	4500	0.8	<0.2	25 maleic acid, 25 phthalic acid, 25 1:3-butylen glycol, 25 1:2-propylene glycol
J	5000	~0.3	~0.9	23 phthalic acid, 27 fumaric acid, 50 1:3-butylen glycol
K	3000	~1.2	<0.3	28 tetrachlorophthalic acid, 21 maleic acid, 25 ethylene glycol, 26 1:3-butylen glycol

The polyesters prepared with the use of maleic acid or maleic acid anhydride have undergone partial molecular rearrangement into fumaric acid types

The conditions for the preparation of the emulsifying agents according to the invention for various combinations given by way of example are summarised in the following table:

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Polyester A	900	900	900	900	900	1000	800	800	1000	2000	2000	2000	1800	1200
B													300	30
C														
D														
E														
F														
G														
H														
J														
K														
Hexamethylene diisocyanate	15	25	44.5	45	20	35	15	40	45	45	40	25	40	1200
Commercial toluylene diisocyanate (isomeric mixture)														
Polyethylene oxide mol. wt.	45	90	190	220	100	150	150	160	180	160	150	200	140	150
" "														
" "														
Ethoxylated oleyl alcohol M 2400														
Toluene														
Styrene														
Ethyl acetate														
Reaction temperature °C	60	50	50	45	60	80	50	50	70	1000	1400	2000	1800	800
Reaction time h	10	22	18	30	15	6	18	25	10	70	55	60	40	45
										15	10	20	18	10

To carry out the reaction, the polyalkylene oxide is dissolved or suspended in the polyester or polyester solution and heated. The isocyanate is then added and the mixture stirred for several hours at elevated temperature.

Soluble, viscous to wax-like products compatible with polyesters of type A—K are obtained in every case.

The reverse emulsifying effect of the products of the process are illustrated in the following tabulated examples:

Example	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Emulsifier according to Example	10	9	10	5	2	9	7	16	30	12	100	10	50	15	10	20	20	
Parts																		
1 "																		
2 "																		
3 "																		
4 "																		
5 "																		
6 "																		
7 "																		
8 "																		
11 "																		
14 "																		
A "																		
F "	40	30		40	65		70	80	70	60		60	50	10	70		60	20
H "						60										20		50
H "						40										80	40	
K "																		
Xylene																		
Styrene	60	70	100	60	35	40	30	20		401		40	50	90	30			50
Methylmethacrylate																		
Perchloroethylene																		
Ethyl acetate																		
Water incorporated in the emulsion	250	400	1000	500	200	450	500	50	100	400	250	700	600	1300	900	400	400	550

To prepare the emulsion, the emulsifying agent is first dissolved in the polyester or the polyester solution, and the water is then stirred into the oil phase, the precautionary measures explained in the preceding text being observed. The process can, of course, also be applied to other types of polyesters provided they conform to the conditions mentioned. For example, experiment 26 can also be carried out with the types of polyester B, C, D, E and G. Stable, creamy water in oil emulsions are obtained in each case. This can be confirmed by demonstrating that a drop of the emulsion will not be distributed in water but behaves like an oil drop, i.e. it will not take up water.

The possibility of polymerising suitable water in oil emulsions prepared with the aid of the emulsifying agents according to the process is illustrated by the following further Examples:

EXAMPLE 33:

350 parts of H_2O were incorporated by emulsification into a solution consisting of 50 parts of polyester J, 60 parts of styrene, 10 parts of emulsifier according to Example 3 and 2.5 parts of benzoyl peroxide. 1.5 parts of N-dimethyl-p-toluidine were then stirred into the stable, creamy water in oil emulsion. The emulsion was then poured into a dish where it hardened overnight at room temperature.

EXAMPLE 34:

500 parts of water were carefully emulsified into a solution consisting of 40 parts of polyester J, 70 parts of methyl methacrylate, 8 parts of emulsifier according to Example 8 and 2 parts of azodiisobutyronitrile. The creamy, stable water in oil emulsion could be hardened at 65° C. to a solid, water-containing polymer mass.

EXAMPLE 35:

A solution of 2 parts of ammonium peroxydisulphate in 100 parts of H_2O followed by a solution of 1 part of sodium disulphite in 100 parts of H_2O was emulsified into a solution consisting of 55 parts of polyester H, 45 parts of styrene and 10 parts of emulsifier according to Example 8. The stable water in oil emulsion obtained hardened overnight at 45° C.

EXAMPLE 36:

10 parts of an addition product of 20 mols. of ethylene oxide and polyester A were dissolved, together with 90 parts of polyester H, in 70 parts of styrene. 10 to 300 parts of H_2O , according to requirement, could be stirred into this solution to form a stable, creamy water in oil emulsion. If 1.5 parts of lauroyl peroxide were added to the organic phase prior to the emulsifying process, the water in oil emulsion could be hardened to solid blocks of polymer at 50 to 75° C.

EXAMPLE 37:

100 parts of polyester A and 10 parts of hexamethylol melamine butyl ether (Maprenal NPTM) and 20 parts of polyethylene oxide of molecular weight 1550 were stirred for 10 hours at 130° C. 10 parts of the resulting product were then dissolved in 100 parts of styrene. 1600 parts of water could be stirred into this solution to form a stable water in oil emulsion. If 10 parts of the resulting product and 50 parts of polyester H were dissolved in 50 parts of styrene, 100 to 680 parts of H_2O could be stirred in to form a stable water in oil emulsion.

EXAMPLE 38:

Procedure was analogous to Example 37 except that polyester C was used instead of polyester A for the preparation of the emulsifier.

EXAMPLE 39:

Procedure was analogous to Example 37 except that instead of hexamethylolmelamine butyl ether, the same quantity of the formaldehyde adduct of 1,2-propylene urea was used for linking the polyester molecule and polyalkylene oxide.

EXAMPLE 40:

100 parts of polyester A were stirred together with 20 parts of polyethylene oxide (molecular weight 1550) and 10 parts of 4,4'-dihydroxydiphenyl - dimethylmethane - diglycidic ether for 12 hours at 130° C. A viscous mass was obtained which was readily soluble in aromatic compounds, esters and polyesters. 10 parts of the reaction product were dissolved in 100 parts of styrene. It was then possible to stir 1700 parts of water into this solution to form a water in oil emulsion. If 10 parts of the reaction product together with 50 parts of polyester H were dissolved in 50 parts of styrene, 5 to 400 parts of water could be stirred into this solution to form a stable water in oil emulsion.

EXAMPLE 41:

Procedure was analogous to Example 40 except that polyester C was used instead of polyester A.

EXAMPLE 42:

Procedure was analogous to Example 40 except that polyester B was used instead of polyester A.

WHAT WE CLAIM IS:—

1. A water-in-oil emulsion having water finely dispersed within a liquid organic phase, said organic phase comprising in a quantity of 1 to 100% by weight a water insoluble or sparingly soluble emulsifying agent which is a reaction product which has a molecular weight of 1,000 to 20,000 of a polyester

- which has a molecular weight of 500 to 10,000 of an organic compound containing at least two hydroxyl groups and an organic carboxylic acid containing at least two carboxyl groups, said polyester having at least one terminal carboxyl group and/or at least one terminal hydroxyl group, and a water-soluble polyalkylene oxide which has a molecular weight between 400 and 10,000.
2. An emulsion as claimed in claim 1 in which the water insoluble emulsifying agent is a water insoluble or sparingly soluble derivative of a water insoluble polyester of a dihydric alcohol and a dibasic carboxylic acid, said polyester having a molecular weight of 500 to 10,000 and having at least one terminal carboxyl and/or at least one hydroxyl group, the hydrogen atoms of said terminal groups being replaced by a radical which is obtained by subtracting a hydroxyl group from the molecule of a water-soluble polyethylene oxide having a molecular weight between 400 and 10,000, and the molecular weight of said emulsifying agent being from 1,000 to 20,000.
3. An emulsion as claimed in claim 1 in which the water insoluble or sparingly soluble emulsifying agent is a water insoluble or sparingly soluble derivative of a water insoluble polyester of dihydric alcohol and dibasic carboxylic acid, said polyester having a molecular weight of 500 to 10,000 and having at least one terminal carboxyl and/or at least one hydroxyl groups, said derivative being the reaction product of (a) said polyester, (b) a water soluble polyethylene oxide having a molecular weight between 400 and 10,000 and (c) an organic compound having two reactive groups which are capable of reacting with the terminal groups of said polyesters and polyethylene oxides, said emulsifying agent having a molecular weight between 1000 and 20,000.
4. A water-in-oil emulsion as claimed in claim 3 in which the polyester having terminal hydroxyl and carboxylic acid groups is the reaction product of (a) one of the following dicarboxylic acids namely: maleic acid, fumaric acid, adipic acid, phthalic acid, terephthalic acid, tetrachlorophthalic acid or a mixture of two or more acids and (b) one of the following dihydric alcohols namely: ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and mixtures of two or more such acids.
5. An emulsion as claimed in claim 3 or claim 4 in which the organic compound having two reactive groups, which are capable of reacting with the terminal groups of said polyesters and polyethylene oxides is one of the following compounds, namely hexamethylene-1,6-diisocyanate, 2,4-toluylene diisocyanate, 2,6-toluylene diisocyanate, mixtures of 2,4- and 2,6-toluylene diisocyanates, hexamethylol melamine butyl ether and 4,4'-dihydroxydiphenyl-dimethylmethane diglycidyl ether.
6. A water-in-oil emulsion having water finely dispersed within a liquid organic phase said liquid organic phase comprising 1) a liquid organic polyester devoid of aliphatic unsaturation, a liquid olefinically unsaturated organic polyester, a liquid olefinically unsaturated organic monomer containing at least one terminal $\text{CH}_2=\text{CH}<$ group, a liquid organic solvent devoid of aliphatic unsaturation, a liquid solution of a polyester in said liquid olefinically unsaturated monomer, or a liquid solution of a polyester in said liquid organic solvent devoid of aliphatic unsaturation, said phase (1) being devoid of emulsifying properties and 2) an emulsifying agent as defined in any of claims 3 to 5 which emulsifying agent is dissolved in said organic phase.
7. Water-in-oil emulsions as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

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